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Highly asymmetric coordination of trimethylsilyl groups to tetrazole and triazole rings: an experimental and computational study in gaseous and crystalline phases†

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1-Trimethylsilyltetrazole, **1**, has been synthesised from chlorotrimethylsilane and tetrazole in the presence of triethylamine as an auxiliary base. The structure of this compound has been determined in the crystalline phase by X-ray diffraction of a crystal grown *in situ*. The gas-phase structures of **1** and 1-trimethylsilyl-1,2,4-triazole, **2**, have been determined by gas-phase electron diffraction (GED). An extensive investigation of these and related compounds by *ab initio* calculations is also reported. The angles between the rings and the substituents on N were of particular interest. It was found that the calculated difference of 15.5° between the CNSi and NNSi angles in **1** was mostly, but not entirely, an inherent property of the tetrazole ring and not due to a short Si...N interaction.

Introduction

Layers of silicon nitride, Si₃N₄, have many applications in materials sciences both as bulk materials for high-performance ceramics¹ and as thin films for use in microelectronic devices.² Layers are often produced by deposition from the gas phase by plasma-enhanced chemical vapour deposition (PECVD)³ of mixtures of N₂ or NH₃ with SiH₄. New single-source precursors are desirable to simplify the deposition process and also to improve safety by employing non-pyrophoric compounds. Organosilicon derivatives of tetrazole have a relatively high nitrogen content compared to carbon content and are, therefore, potential candidates for single-source precursors of silicon nitride thin films.

Through our work on this topic it became apparent that the structural chemistry of silyltetrazoles has not been investigated in great depth. Consequently, we have determined the crystal structure of 1-trimethylsilyltetrazole, **1**, (first synthesised by Birkofer *et al.* in 1963)⁴ by X-ray diffraction of a crystal grown *in situ*, as well as the structure in the gas phase by electron diffraction (GED). For comparison, the GED structure of 1-trimethylsilyl-1,2,4-triazole, **2**, has also been determined. *Ab initio* calculations have been performed for both compounds, as well as for a number of related compounds.

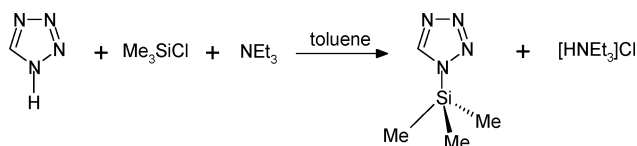
Experimental

Synthesis

The preparation of **1** followed a procedure modified from that described by Birkofer *et al.*⁴ and was carried out under dry

nitrogen. The toluene and triethylamine were dried over CaH₂ and distilled prior to use. All glassware was heated to 160 °C, evacuated and filled with dry nitrogen before use.

As shown in Scheme 1, triethylamine (6.16 ml, 48 mmol) was added to a solution of tetrazole (3.4 g, 48 mmol) in 30 ml anhydrous toluene. The mixture was cooled to 10 °C and a solution of chlorotrimethylsilane (6.1 ml, 48 mmol) in 10 ml toluene was added dropwise over 15 min. The reaction mixture was stirred for 24 h at 0 °C, filtered, and the toluene was distilled off. Fractional distillation yielded 2 ml (yield 37.5%) of **1** with bp 55 °C (0.1 Torr), mp 28 °C. The compound is sensitive to hydrolysis, but can be stored at room temperature under nitrogen for several months.



Scheme 1 Preparation of **1**.

¹H NMR (C₆D₆, 500 MHz) δ 0.51 (s, 9H, CH₃), 8.62 (s, 1H, CH). ¹³C{¹H} NMR (C₆D₆, 50.33 MHz) δ -2.2 (s, CH₃), 148.37 (s, NCN). ²⁹Si NMR (C₆D₆, 99.30 MHz) δ 22.26 (s, SiCH₃). IR (Midac Prospect FT/IR, film) ν = 3125, 2965, 1465, 1259, 1167, 1072, 1016, 858, 769, 673 cm⁻¹.

A sample of **2** (stated purity ≥ 97%) was purchased from Aldrich and used without further purification.

Computational

Ab initio calculations were performed for **1** and **2** and for several related molecules using the Gaussian 03 suite of programs.⁵ Geometry optimisations were performed using a variety of theories and basis sets ranging from RHF/3-21G* to MP2/6-311++G(3df,3pd).⁶⁻⁹ All MP2 calculations were of the frozen core type. Harmonic force constants calculated at the RHF/6-31G*

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† Electronic supplementary information (ESI) available: Tables S1–S21 and Fig. S1–S2. CCDC reference number 679183. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b803091j

level were subsequently used along with the program SHRINK¹⁰ to obtain initial amplitudes of vibration and curvilinear perpendicular distance correction terms for use in the GED refinement. Potential-energy scans relating to some angles were calculated at the RHF/6-31G* level.

Gas-phase electron diffraction (GED)

Data were collected for **1** and **2** using the Edinburgh gas electron diffraction apparatus,¹¹ using an accelerating voltage of *ca.* 40 kV (*ca.* 6.0 pm electron wavelength) on Kodak Electron Image film. Nozzle-to-film distances were determined using benzene vapour as a standard, the images taken immediately after recording the diffraction patterns of **1** and **2**. The electron-scattering patterns were converted into digital form using an Epson Expression 1680 Pro flatbed scanner with a scanning program described elsewhere.¹² Data reduction and least-squares refinements were carried out using the ed@ed program,¹³ employing the scattering factors of Ross *et al.*¹⁴ Details of temperatures, nozzle-to-film distances, scale factors, *s* limits, weighting points, correlation parameters and electron wavelengths are given in Table S1 (see ESI†).

X-Ray crystallography†

A single crystal was obtained by *in situ* crystallisation in a Duran glass capillary, mounted directly onto the goniometer of an Enraf Nonius CAD4 X-ray diffractometer. Data were collected at 133(2) K with graphite-monochromated Mo K α radiation. The structure was solved using the SHELXTL 5.01 program system and refined by full-matrix least-squares methods. The cell parameters are as follows: space group *P*2₁, monoclinic, *a* = 5.916(1), *b* = 10.577(1), *c* = 6.624(1) Å, β = 105.35(1)°. Non-hydrogen atoms were refined anisotropically, whilst the hydrogen atom attached to C(5) was refined freely and isotropically. The other hydrogen atoms were placed in idealised positions, based on the Si–C–H angles, and refined with a common C–H distance for every methyl group and free conformational parameter. Using 1628 of the 2397 measured scattering intensities (R_{int} = 0.094) the refinement converged to R_1 = 0.0470 (for 1430 data with $I > 2\sigma(I)$, wR_2 = 0.1193 for all 1628 data); the largest difference peak and hole are 0.31 and –0.28 e Å^{–3}, respectively.

Results

Calculated structures of the title compounds

Both **1** and **2** have *C*_s-symmetric structures with one Si–C bond eclipsing an N–C ring bond. See Fig. 1 for molecular structures, including the atom-numbering scheme. Frequency calculations (RHF/6-31G*) for **1** and **2** revealed that the lowest-lying vibrational frequencies (*ca.* 40 cm^{–1}) correspond to torsions about the N–Si bonds. These calculations prompted searches of the N–N–Si–C(7) torsional potentials (RHF/6-31G*), confirming that the energy minima for both **1** and **2** represent conformers with N–N–Si–C(7) = 180°, and that the energy barriers to rotation are approximately 4 and 6 kJ mol^{–1}, respectively (Fig. 2).

Many geometry optimisations were performed in order to assess the effects of increasing the basis-set size and raising the quality of theory. Coordinates and energies for **1** and **2** calculated at the MP2/6-311++G(3df,3pd) level are given in Tables S3 and

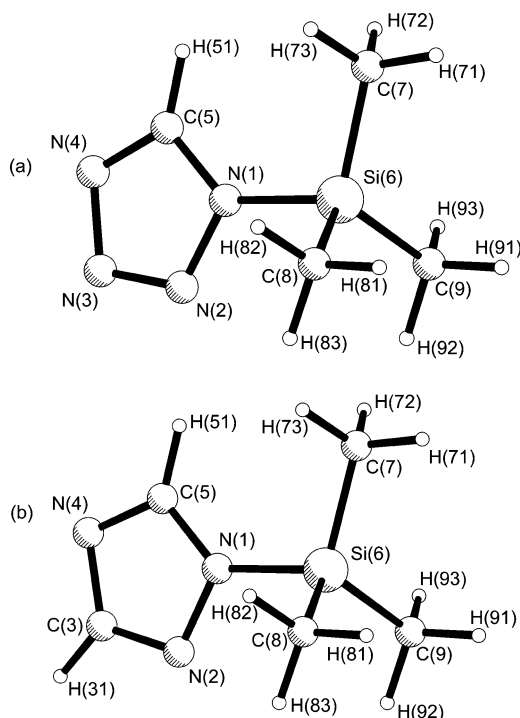


Fig. 1 Gas-phase molecular structures of (a) **1** and (b) **2** showing atom numbering.

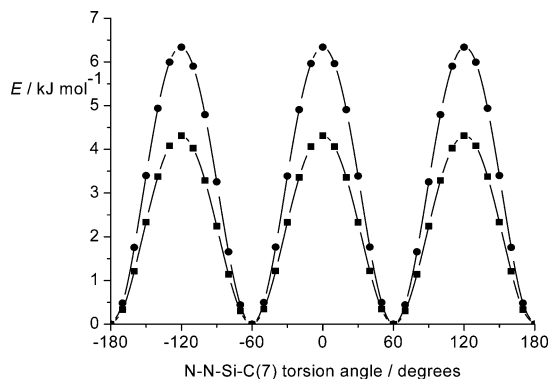


Fig. 2 Calculated (RHF/6-31G*) energies for rotation around the N–Si bond of 1-trimethylsilyltetrazole (**1**, ■) and 1-trimethylsilyl-1,2,4-triazole (**2**, ●).

S4.† For **1**, significant changes in bond lengths were observed at the RHF level on moving from the 3-21G* to the 6-31G* basis set. This was most pronounced within the tetrazole ring, resulting in a shortening of the N(3)–N(4) bond by just over 7 pm. Significant increases in ring bond lengths were also observed on the introduction of electron correlation *via* MP2 theory. As expected, these effects were most pronounced in the bonds with most π -bonding character, namely the N(4)–C(5) and N(2)–N(3) bonds, which lengthened by 3.8 and 7.3 pm respectively. The other ring distances also exhibited significant lengthening: N(3)–N(4) by 2.1 pm; N(1)–C(5) by 1.9 pm and N(1)–N(2) by 2.3 pm. In contrast to the fluctuations in bond length within the ring, the lengths of the bonds involving the silicon atom remained reasonably constant, although the N(1)–Si distance was lengthened by 1.7 pm on introduction of electron correlation (MP2 theory).

The largest changes in bond angles were observed upon the introduction of electron correlation, although the majority of these changes were less than 0.5° . Bond angles involving silicon appeared to be the most affected, the largest deviation being the angle N(2)–N(1)–Si, which narrowed by 1.8° . However, some ring angles were also affected, including N(2)–N(1)–C(5) and N(1)–N(2)–N(3), which widened by 1.4° and narrowed by 1.1° , respectively. These bond angles subsequently varied by no more than 0.2° on increasing the basis set size from 6-31G* to 6-311++G(3df,3pd). In contrast to the bond lengths and angles, the torsion angles showed little variation on increasing the level of theory and basis set from the values computed at the RHF/3-21G* level.

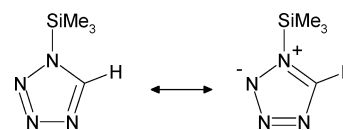
Very similar trends were observed for **2**, although the replacement of N in the ring by a CH fragment meant that the effects of theory and basis set on the ring parameters were less pronounced.

Calculated structures of related molecules

The calculated C(5)–N(1)–Si angle in **1**, which converged to 134.2° , is of interest because it is much wider than the adjacent N(2)–N(1)–Si angle (118.7°). To investigate this large displacement of the silicon atom away from the carbon and towards the nitrogen atom, the related structures of tetrazole, 1-silyltetrazole, trimethylsilylpentazole and 1-*tert*-butyltetrazole were investigated using similar series of graded calculations. Each was calculated at the MP2/6-311++G** level; coordinates for each molecule are given in Tables S5–S8.†

It was observed that 1-silyltetrazole has a calculated C–N–Si angle of 133.5° and N–N–Si angle of 119.5° , angles very similar to those in the trimethylsilyl analogue. Tetrazole also has a C–N–H angle (130.6°) that is much wider than N–N–H (120.1°). Replacing the Si atom in **1** by carbon leads to 1-*tert*-butyltetrazole. In this compound the steric bulk of the substituent is comparable to that in **1**, but the lack of a silicon atom means that no Si...N interaction is possible. It is therefore interesting to note that we still observe a much wider C–N–C angle (131.8°) in 1-*tert*-butyltetrazole compared to its N–N–C angle (120.0°). Taking all these observations into account it appears that of the 15.5° difference between the C–N–Si and N–N–Si angles in **1**, about 1.5° can be attributed to the effects of the three methyl groups and about 4° to the presence of the silicon atom. The remaining 10° appears to be an inherent property of the tetrazole ring. A completely satisfactory explanation for these observations has not been found, but they may be due to the difference in electronegativity between C and N atoms. In the case of trimethylsilylpentazole, in which a CH moiety has been replaced by a nitrogen atom, the two NNSi angles are, of course, equal, at 124.2° , as the situation about the silylated ring atom is symmetric. However, in the 1-substituted tetrazole case, the C–N bond is more polar than the N–N bond. The strongest repulsion about the silylated N atom in terms of an VSEPR model is thus that between the C–N and the Si–N bonds, leading to an increase of the SiNC angle and a concomitant decrease of the SiNN angle.

Scheme 2 shows the most likely mesomeric forms of **1**. If the form on the right-hand side did contribute to the overall structure of **1**, we would expect to see a wide CNSi angle and a narrow NNSi angle. Overall, it is not possible to provide a single, simple explanation for the asymmetry of the coordination of the silyl



Scheme 2 Mesomeric forms of **1**.

groups in these compounds, but it appears that the largest part of the effect arises from properties of the ring, and is not specific to the silyl groups.

GED refinements

Very similar models were used to describe **1** and **2**, with one extra refineable parameter used to position the additional hydrogen atom in **2**. The planar tetrazole ring in **1** and the planar triazole ring in **2** imply local C_s symmetry, whilst the SiMe₃ groups were allowed to rotate, giving the models overall C_1 symmetry.

For brevity only the model for **1** will be described. That for **2** was identical [with C(3) replacing N(3)] except where the extra H atom is concerned. The independent geometric parameters used are listed in Table 1. The Si–N and three Si–C distances were calculated to be very similar and so were described using the average of the four and three difference parameters (p_{1-4}) as follows:

$$p_1 = [r_{\text{Si-N}} + r_{\text{Si-C(7)}} + r_{\text{Si-C(8)}} + r_{\text{Si-C(9)}}]/4$$

$$p_2 = r_{\text{Si-N}} - [r_{\text{Si-C(7)}} + r_{\text{Si-C(8)}} + r_{\text{Si-C(9)}}]/3$$

$$p_3 = r_{\text{Si-C(7)}} - [r_{\text{Si-C(8)}} + r_{\text{Si-C(9)}}]/2$$

$$p_4 = r_{\text{Si-C(8)}} - r_{\text{Si-C(9)}}$$

Similarly the N–N and N–C distances around the ring were described using the average and four differences (p_{5-9}):

$$p_5 = [r_{\text{N(1)-N(2)}} + r_{\text{N(2)-N/C(3)}} + r_{\text{N/C(3)-N(4)}} + r_{\text{N(4)-C(5)}} + r_{\text{C(5)-N(1)}}]/5$$

$$p_6 = \{[r_{\text{N(1)-N(2)}} + r_{\text{N/C(3)-N(4)}} + r_{\text{C(5)-N(1)}}]/3\} - \{[r_{\text{N(4)-C(5)}} + r_{\text{N(2)-N/C(3)}}]/2\}$$

$$p_7 = r_{\text{N(4)-C(5)}} - r_{\text{N(2)-N/C(3)}}$$

$$p_8 = \{[r_{\text{N(1)-N(2)}} + r_{\text{C(5)-N(1)}}]/2\} - r_{\text{N/C(3)-N(4)}}$$

$$p_9 = r_{\text{N(1)-N(2)}} - r_{\text{C(5)-N(1)}}$$

The C–H distances in the methyl groups were different to that for the hydrogen attached to the ring (two on the ring in the case of **2**) and the average of all C–H distances and the difference between the methyl and ring distances were used (p_{10-11}). Tiny differences between distances within these two groups were ignored.

The set of three N–Si–C angles was, for completeness, described using average and difference parameters (p_{12-14}) as were the two C–Si–C angles (p_{15-16}) required to complete the positioning of the methyl carbon atoms. The Si–C–H angles were calculated to be very similar and so were described by a single value (p_{17}). The C–N–Si, C–N–N and N–N–N angles completed the description of the ring along with N(1)–C(5)–H (p_{18-21}). A torsion angle (p_{22}) was used to describe the rotation of the SiMe₃ group, where a value of 0° represented $\phi\text{C(7)-Si(6)-N(1)-C(3)} = 0^\circ$ and a positive value was given for a clockwise rotation when viewed from Si to N. Parameter 23, which is only relevant for **2**, was N(2)–C(3)–H. As the calculations showed that the methyl groups were always staggered, these were fixed in the models.

All of the parameters defined for each of **1** and **2** were allowed to refine. Where parameters refined to unrealistic values flexible restraints were applied using the SARACEN method.¹⁵ The uncertainty of a restraint relates to the degree of convergence of the calculated values for that parameter in the series of calculations

Table 1 Calculated and GED geometric parameters for **1** and **2**.^{a,b}

Parameters	1			2		
	r_{H1}	MP2 ^c	Restraint uncertainty	Value	MP2 ^c	Restraint uncertainty
<i>Independent</i>						
p_1 rSi–N/C average	183.20(7)	184.4	—	183.76(9)	184.2	—
p_2 rSi–N/C difference 1	–6.4(4)	–4.8	0.5	–6.2(5)	–6.3	0.5
p_3 rSi–N/C difference 2	0.5(5)	0.6	0.5	5.4(5)	0.6	0.5
p_4 rSi–N/C difference 3	0.0(5)	0.0	0.5	0.0(5)	0.0	0.5
p_5 rN–N/C average	132.30(7)	133.8	—	134.45(8)	134.6	—
p_6 rN–N/C difference 1	4.2(5)	3.0	0.5	2.8(5)	2.8	0.5
p_7 rN–N/C difference 2	0.6(5)	0.6	0.5	–0.7(5)	–0.9	0.5
p_8 rN–N/C difference 3	–0.4(5)	0.0	0.5	0.2(5)	0.2	0.5
p_9 rN–N/C difference 4	1.3(5)	0.2	0.5	0.0(5)	0.4	0.5
p_{10} rC–H average	107.2(3)	108.3	0.5	106.9(3)	108.4	—
p_{11} rC–H difference	1.0(5)	1.5	0.5	1.2(5)	1.3	0.5
p_{12} \angle N–Si–C average	106.1(3)	105.5	—	110.3(3)	106.1	—
p_{13} \angle N–Si–C difference 1	–1.2(5)	–1.5	0.5	–1.4(5)	–1.7	0.5
p_{14} \angle N–Si–C difference 2	0.0(5)	0.0	0.5	0.0(5)	0.0	0.5
p_{15} \angle C–Si–C average	112.4(11)	113.2	1.0	115.5(6)	112.7	1.0
p_{16} \angle C–Si–C difference	0.0(5)	0.0	0.5	0.0(5)	0.0	0.5
p_{17} \angle Si–C–H average	111.7(5)	110.7	1.0	111.4(4)	110.5	1.0
p_{18} \angle C–N–Si	131.0(4)	134.2	0.5	132.1(6)	133.2	—
p_{19} \angle C(5)–N(1)–N(2)	107.9(4)	107.1	—	107.6(9)	108.6	—
p_{20} \angle N(1)–N(2)–N/C(3)	106.1(4)	106.9	—	103.8(8)	102.9	—
p_{21} \angle N(1)–C(5)–H	124.4(11)	124.4	1.0	123.1(10)	122.9	1.0
SiMe ₃ torsion	0.0(1)	0.0	—	0.0(2)	0.0	—
p_{23} \angle N(2)–C(3)–H in 2	—	—	—	123.6(10)	121.4	1.0
<i>Dependent</i>						
$r_{\text{N}(1)\text{--N}(2)}$	134.5(4)	135.2	—	135.6(4)	136.0	—
d_2 $r_{\text{N}(2)\text{--N/C}(3)}$	129.5(4)	131.7	—	133.2(4)	133.4	—
d_3 $r_{\text{N/C}(3)\text{--N}(4)}$	134.3(4)	135.0	—	135.4(4)	135.6	—
d_4 $r_{\text{N}(4)\text{--C}(5)}$	130.1(4)	132.3	—	132.5(4)	132.5	—
d_5 $r_{\text{C}(5)\text{--N}(1)}$	133.2(4)	134.8	—	135.6(4)	135.6	—
d_6 $r_{\text{Si--N}}$	178.4(4)	180.8	—	179.1(4)	179.5	—
d_7 $r_{\text{Si--C}(7)}$	185.1(4)	186.0	—	185.7(4)	186.2	—
d_8 $r_{\text{Si--C}(8)}$	184.6(4)	185.4	—	185.1(3)	185.6	—
d_9 $r_{\text{Si--C}(9)}$	184.6(4)	185.4	—	185.1(3)	185.6	—
d_{10} \angle N–N–Si	121.1(4)	118.7	—	119.9(9)	118.2	—
d_{11} \angle N(2)–N/C(3)–N(4)	110.8(4)	110.6	0.5	114.5(7)	115.0	—
d_{12} \angle N/C(3)–N(4)–C(5)	106.2(3)	105.7	0.5	102.4(7)	102.4	—
d_{13} \angle N(4)–C(5)–N(1)	109.0(4)	109.7	0.5	111.5(9)	111.1	—

^a All distances (r) are in pm, all angles (\angle) and dihedral angles are in degrees. See text for parameter definitions and Fig. 1 for atom numbering. ^b Figures in parentheses are the estimated standard deviations of the last digits. ^c 6-311++G(3df,3pd) basis set.

using different methods and basis sets. In the case of **1** and **2** these were less than 1 pm and 1° for all distances and angles, respectively, and less than 0.5 pm and 0.5° for associated differences. The uncertainties placed on these restraints are given in Table 1. For each of **1** and **2** a total of 14 groups of vibrational amplitudes were also refined. When amplitude values refined to unrealistic values restraints were also applied using the SARACEN method.¹⁵ Despite this some amplitudes of vibration continued to be larger or smaller than calculated values; this reflects the experimental data, and the SARACEN method does not force the calculated values to override the experiments. Fixing the amplitude of vibration for N(3)–N(5) in **1** at its calculated value, for example, had a negligible effect on the ring structure. Complete lists of distances, with corresponding refined amplitudes of vibration (u) and perpendicular distance corrections (k), are available as supplementary information (Tables S9 and S10).[†]

The successes of the final refinements can be gauged by the R_{G} factors of 0.083 ($R_{\text{D}} = 0.037$) for **1** and 0.073 ($R_{\text{D}} = 0.045$) for **2**. The quality of fit can also be assessed in terms of the radial-distribution

curves (Fig. 3) and molecular-scattering intensity curves (Fig. S1 and S2).[†] These show good agreement between the model and experimental data, indicated by the difference curves. Coordinates from the final GED structures of **1** and **2** are given in Tables S11 and S12 and least-squares correlation matrices are given in Tables S13 and S14.[†]

Crystal structure

Compound **1** crystallised in the monoclinic space group $P2_1$, with two molecules in the unit cell. Important structural parameters are listed in Table 2, where they are compared to theoretical values and those from GED. The unit cell is depicted in Fig. 4. Fractional coordinates for the crystal structure and anisotropic displacement parameters are given in Tables S15–S17.[†] Full lists of bond lengths, bond angles and torsional angles are given in Tables S18–S19.[†]

In the crystal structure of **1** the CN₄ ring is virtually planar and the silicon atom lies slightly out of the plane of the ring. A weak C–H⋯N hydrogen bond¹⁶ [244(4) pm] between N(2) of one molecule

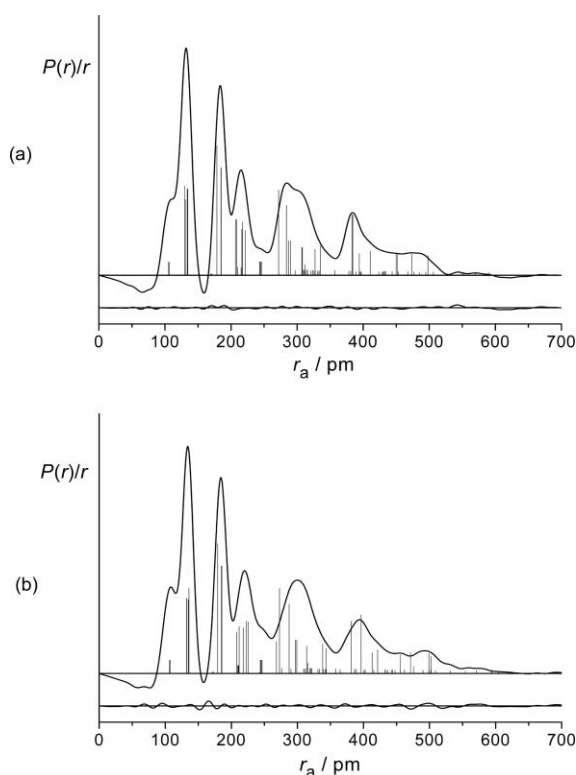


Fig. 3 Experimental and difference (experimental minus theoretical) radial-distribution curves, $P(r)/r$, for (a) **1** and (b) **2**. Before Fourier inversion the data were multiplied by $s \exp[(-0.0002s^2)/(Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{N}} - f_{\text{N}})]$.

Table 2 Comparison of some experimental and theoretical parameters for 1-trimethylsilyltetrazole, **1**, and 1-trimethylsilyl-1,2,4-triazole, **2**^a

	1			2		
	X-Ray	GED (r_{hl})	MP2 ^b	GED (r_{hl})	MP2 ^b	
N(1)–N(2)	135.7(4)	134.5(4)	135.2	135.6(4)	136.0	
N(2)–N/C(3)	127.8(5)	129.5(4)	131.7	133.2(4)	133.4	
N/C(3)–N(4)	134.3(5)	134.3(4)	135.0	135.4(4)	135.6	
N(4)–C(5)	130.9(5)	130.1(4)	132.3	132.5(4)	132.5	
C(5)–N(1)	133.7(4)	133.2(4)	134.8	135.6(4)	135.6	
Ring distance average	132.5	132.3(1)	133.8	134.5(1)	134.6	
N(1)–Si	182.4(3)	178.4(4)	180.8	179.1(4)	179.5	
N(1)–C(5)–N(4)	111.3(3)	109.0(4)	109.7	111.5(9)	111.1	
C(5)–N(1)–N(2)	105.5(2)	107.9(4)	107.1	107.6(9)	108.6	
N(1)–N(2)–N/C(3)	107.0(3)	106.1(4)	106.9	102.4(7)	102.9	
N(4)–N/C(3)–N(2)	112.3(4)	110.8(4)	110.6	114.5(7)	115.0	
C(5)–N(4)–N/C(3)	103.9(4)	106.2(3)	105.7	102.4(7)	102.4	
C(5)–N(1)–Si	132.4(2)	131.0(4)	134.2	132.1(7)	133.2	
N(2)–N(1)–Si	121.9(2)	121.1(4)	118.7	119.9(7)	118.2	
C–N–Si minus N–N–Si	10.5	9.9	15.5	12.2	15.0	
N–N–Si–C(7)	203.6(4)	180.0(1)	180.0	180.0(2)	180.0	

^a Distances are in pm and angles and torsional angles in degrees. ^b 6-311+G(3df,3pd) basis set.

and H(51) of a neighbouring molecule has been identified. [The C...N distance is 328.9(4) pm, the C–H distance 92(4) pm, the C–H...N angle 154(4)°.] This might account for the orientation of the trimethylsilyl group relative to the N–C bond [C(7)–Si–N–C = 30.1(3)°], which represents a twist of the trimethylsilyl group that is not observed for the gas-phase or calculated structures.

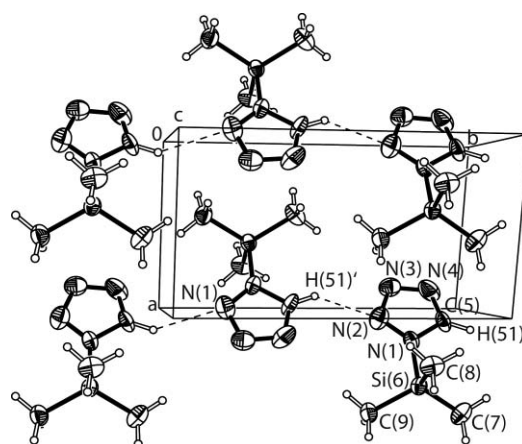


Fig. 4 Crystal structure of **1** showing the C–H...N hydrogen-bonding motif and the aggregation into chains. The thermal ellipsoids are shown at the 50% probability level.

The observed Si–C (mean value 184.0 pm) and Si–N bond lengths [182.4(2) pm] are unsurprising and do not differ significantly from those in similar silicon compounds. The bond length N(2)–N(3) is, at 127.7(5) pm, somewhat shorter than that in the gas phase at 129.5(4) pm, but the other structural parameters are similar in the gaseous and crystalline phases.

Discussion

The molecular structures of 1-trimethylsilyltetrazole, **1**, and 1-trimethylsilyl-1,2,4-triazole, **2**, have been studied in the gas phase by electron diffraction and *ab initio* calculations, and **1** has also been studied in the crystalline phase by X-ray diffraction. The values of important geometric parameters are compared in Table 2.

Despite the high degrees of convergence of the calculated geometries of **1** and **2**, some differences were observed between these and the GED structure. The bond angles in the tetrazole ring of **1** were quite poorly defined by GED. Without SARACEN restraints the angles deviated from their *ab initio* values by up to 7°. This is a common problem with five-membered rings, for which all non-bonded (cross-ring) distances are similar, so the GED data provide insufficient information. Based on the degree of convergence of the calculations this seemed completely unreasonable and therefore restraints were imposed as described in Table 1. With these restraints in place the refinement yielded much more acceptable values.

The differences between the C–N–Si and N–N–Si angles were calculated to be 15.5° for **1** and 15.0° for **2**, but were smaller in the GED structures (see Table 2). In an attempt to understand why the theoretical C–N–Si angle was wider than the experimental value in **1**, a geometry optimisation (MP2/6-311+G*) was performed with the C–N–Si angle fixed at the GED value. (The coordinates for this calculated geometry are given in Table S20.)† The resulting increase in energy was found to be only 0.7 kJ mol^{−1}. This is easily surmountable at experimental temperatures, so there may be vibrational effects not accounted for, even at the r_{hl} level of vibrational treatment. Alternatively, even higher-level calculations could lead to significant changes in the calculated parameters.

Potential-energy curves for rotation about the Si–N bond were calculated and plotted for both **1** and **2**. As shown in Fig. 2, the

barrier to rotation is greater by approximately 2 kJ mol⁻¹ for **2**. As **1** and **2** are structurally similar, this phenomenon must be due to the effect of changing the remote N(3) to C(3)H.

The most noticeable difference between the structure of **1** in the crystalline phase and in the gas phase was the torsion angle of the SiMe₃ group. In the gas phase the C(7)–Si–N–C angle was 0.0(1)°, whereas in the crystal this angle was 30.2(4)°. A second more subtle difference is that in the crystal the silicon atom lies out of the plane of the tetrazole ring, resulting in the N(3)–N(2)–N(1)–Si torsion angle deviating from 180° by 5.3°. Initially this appeared to be the immediate result of weak hydrogen bonding, as a short contact (245.6 pm) is observed between N(4) and H(51) in adjacent molecules. If this was the case *ab initio* calculations on a isolated molecule would neglect this effect. However, when a geometry optimisation was performed (MP2/6-311+G*) with the C(7)–Si–N–C angle fixed at 30.2°, a similar deviation in the N(3)–N(2)–N(1)–Si torsion angle (7.2°) was predicted, indicating that this effect is mostly electronic. (The coordinates for this calculated geometry are given in Table S21.)† The out-of-plane Si atom is probably a consequence of the twisted SiMe₃ group, which itself is likely to be due to the weak C–H···N bonding in the solid.

The N–Si distance in the solid-state structure of **1** [182.4(3) pm] was longer than in the gas phase [178.4(8) pm], while the calculated value lay at an intermediate value. The equivalent values in Me₃SiNMe₂ are 171.94(12) pm in the crystal and 171.0(5) pm in the GED structure.¹⁷ That the distance in the crystal structure of **1** is longer than that in Me₃SiNMe₂ seems reasonable because the lone pair on the nitrogen atom is also involved in the ring π system and not only in hyperconjugation to Si. There is no obvious reason for the N–Si distance in **1** to be longer in the crystal than in the gas-phase structure, although this is also the case in Me₃SiNMe₂.

Conclusion

The determination of the structure of 1-trimethylsilyltetrazole, **1**, in both the solid and the gas phase, and 1-trimethylsilyl-1,2,4-triazole, **2**, in the gas phase has demonstrated that weak C–H···N hydrogen bonds can lead to subtle changes in the conformations of molecular compounds, while leaving other secondary interactions almost unaffected. Such a weak secondary interaction is the Si···N interaction between an exocyclic Si atom and an N atom involved in a five-membered ring system. This is demonstrated by the difference between the C(5)–N(1)–Si and N(2)–N(1)–Si angles in comparison with the corresponding angles in the structure of 1-*tert*-butyltetrazole. The effects of nitrogen atoms in aromatic rings are of course much smaller than the Si···N interactions between endocyclic Si atoms and exocyclic N atoms in 1-(*N,N*-dimethylamino)-1-aza-2,5-disilacyclopentane¹⁸ and more generally the Si···N interactions investigated while gaining a better understanding of the α effect in silicon chemistry in various SiON,¹⁹ SiNN²⁰ and SiCN²¹ compounds.

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